

DOCKET NO: 260087US0PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :
MASANORI SERA, ET AL. : EXAMINER: NUTTER, NATHAN M.
SERIAL NO: 10/511,099 :
FILED: JUNE 9, 2005 : GROUP ART UNIT: 1796
FOR: THERMOPLASTIC RESIN :
COMPOSITION :

DECLARATION UNDER 37 C.F.R. § 1.132

COMMISSIONER FOR PATENTS
ALEXANDRIA, VIRGINIA 22313

SIR:

Now comes Shinichi Yukimasa who states that:

1. I graduated with a Master's degree from the Tokyo Institute of Technology in 1993.
2. I have been employed by Idemitsu Kosan Co., Ltd. for 16 years as a scientific researcher in the field of polymer chemistry, with an emphasis on polypropylene and α -olefin polymers.
3. I understand the English language, or at least the contents of the Declaration were made clear to me prior to executing the same.
4. The following experiments were carried out by me or under my direct supervision and control.
5. Measurement of Melting Point (T_m)

By using a differential scanning calorimeter (DSC-7 made by Perkin-Elmer Corp.), a sample was kept at 190°C for 5 minutes, cooled to -10°C at 5°C/minute, kept at -10°C for 5 minutes, and then heated to

190°C at 10°C/minute, to obtain a melting endotherm curve. The temperature corresponding to the peak top in the melting endotherm curve was defined as a melting point (T_m).

6. Measurement of Stereoregularity Index M2 (molc %)

The stereoregularity index M2 was measured according to the method set forth in T. Asakura, M. Demura, and Y. Nishiyama, *Macromolecules*, 24, 2334 (1991), as described at page 56, line 4 to page 57, line 9 of the present specification.

7. Measurement of Miscibility (R)

The miscibility of the thermoplastic resin composition was measured according to the method described at page 57, line 10 to page 59, line 18 of the present specification.

8. Measurement of Film Impact Strength

The film impact strength of each sample was measured according to the method described at page 59, lines 19-23 of the present specification.

9. Preparation of Metallocene Catalyst

Production of (1,2'-dimethylsilylene) (2,1'-dimethyl-silylene) bis(3-trimethylsilylmethylindenyl) zirconium dichloride

Under a nitrogen gas stream, 2.5 g (7.2 mmol) of the (1,2'-dimethylsilylene) (2,1'-dimethylsilylene) bis(indene) and 100 mL of ether were added to a 200-mL Schlenk tube.

The mixture was cooled to -78°C, and thereto was added 9.0 mL of a 1.6 M/L concentration of hexane solution of n-butyllithium (n-BuLi) (14.8 mmol).

The mixture was stirred at the room temperature for 12 hours.

The solvents were distilled off, and the obtained solid was washed with 20 mL of hexane and dried under reduced pressure to obtain a white solid of a lithium salt quantitatively.

In a Schlenk tube, 6.97 mmol of the lithium salt of (1,2'-dimethylsilylene) (2,1'-dimethylsilylene) bis(indene) was dissolved in 50 mL of THF. 2.1 mL (14.2 mmol) of iodomethyltrimethylsilane was slowly added to the solution dropwise at the room temperature, and stirred for 12 hours.

Then, the solvent was distilled off, and washed with a saturated ammonium chloride solution after adding 50 mL of ether.

After the water phase was separated, the organic phase was dried to remove the solvent, thereby obtaining 3.04 g (5.9 mmol) of (1,2'-dimethylsilylene) (2,1'-dimethylsilylene) bis(3-trimethylsilylmethylindene) (84% yield).

Next, under a nitrogen gas stream, 3.04 g (5.9 mmol) of the above (1,2'-dimethylsilylene) (2,1'-dimethylsilylene) bis(3-trimethylsilylmethylindene) and 50 mL of ether were added to a Schlenk tube.

The mixture was cooled to -78°C, and thereto was added 7.4 mL of a 1.6 M/L concentration of n-BuLi hexane solution (11.8 mmol). The resulting mixture was stirred at the room temperature for 12 hours.

The solvents were distilled off, and the resultant solid was washed with 40 mL of hexane to obtain 3.06 g of a lithium salt as an ether adduct.

Results of ¹H-NMR measurement (90 MHz, THF-d₅) of the product were as follows: δ 0.04 (s, -SiMe₃, 18H), 0.48 (s, -Me₂Si-, 12H), 1.10 (t, -CH₃, 6H), 2.59 (s, -CH₂-, 4H), 3.38 (q, -CH₂-, 4H), 6.2-7.7 (m, Ar-H, 8H).

3.06 g of the obtained lithium salt was suspended in 50 mL of toluene under a nitrogen gas stream.

The suspension was cooled to -78°C, and to this was added dropwise a suspension of 1.2 g (5.1 mmol) of zirconium tetrachloride and 20 mL of toluene, which was cooled to -78°C beforehand.

After the addition, the resulting liquid was stirred at the room temperature for 6 hours.

The solvents were distilled off from the reaction mixture, and the residue was recrystallized from dichloromethane to obtain 0.9 g (1.33 mmol) of yellow crystallites of (1,2'-dimethylsilylene) (2,1'-dimethylsilylene)-bis(3-trimethylsilylmethylindenyl) zirconium dichloride (26% yield).

The results of ¹H-NMR measurement (90 MHz, CDCl₃) of the product were as follows: δ 0.0 (s, -SiMe₃-, 18H), 1.02, 1.12 (s, -Me₂Si-, 12H), 2.51 (dd, -CH₂-, 4H), 7.1-7.6 (m, Ar-H, 8H).

10. Experiment: Example 1

Polymerization of 1-octadecene using the Metallocene Catalyst described above

A 1-L autoclave was heat-dried, and thereto were added 200 mL of heptane, 200 mL of 1-octadecene (C_{18}), 0.5 mmol of triisobutylaluminum. After the autoclave was stirred and heated up 80 °C, 25 μ mol of dimethylanilinium borate, 5 μ mol of metallocene catalyst described above were added to the autoclave. Then, hydrogen was introduced into the autoclave at 0.8 MPa, and the polymerization reaction was conducted at the polymerization temperature of 80°C for 120 minutes.

After completion of the polymerization reaction, operation of the re-precipitation was repeated using acetone to deposit a reaction-product, which was dried by heating under a reduced pressure to obtain 121.1 g of a higher α -olefin (C_{18}) polymer (1).

M2 of the obtained higher α -olefin polymer (1) was 60.4 mol % and Tm was 41.5°C, as shown in Table A below.

11. Experiment: Example 2

Polymerization of 1-octadecene using the Metallocene Catalyst described above

A 1-L autoclave was heat-dried, and thereto were added 200 mL of heptane, 200 mL of 1-octadecene (C_{18}), 0.5 mmol of triisobutylaluminum. After the autoclave was stirred and heated up 120 °C, 25 μ mol of dimethylanilinium borate, 5 μ mol of metallocene catalyst described above were added to the autoclave. Then, hydrogen was introduced into the autoclave at 0.9 MPa, and the polymerization reaction was conducted at the polymerization temperature of 120°C for 60 minutes.

After completion of the polymerization reaction, operation of the re-precipitation was repeated using acetone to deposit a reaction-product, which was dried by heating under a reduced pressure to obtain 118.2 g of a higher α -olefin (C_{18}) polymer (2).

M2 of the obtained higher α -olefin polymer (2) was 50.8 mol % and Tm was 40°C, as shown in Table A below.

12. Preparation of Solid Titanium-based Ziegler-Natta Catalyst Component

A three-necked flask, having 0.5 L in volume and provided with a stirrer, for use in preparation of a solid titanium-based Ziegler-Natta catalyst component was purged with a nitrogen gas. After that, 80 ml of dehydrated heptane and 4.0 g (35 mmol) of dehydrated magnesium diethoxide were added to the flask. After heating of the flask up to 80°C, 13.2 mmol of n-dibutyl phthalate added thereto. The solution, thus obtained in the flask was kept at 80°C and 116 ml (1.06 mol) of titanium tetrachloride was added to the flask, and then the flask was stirred for two hours at 110°C in the flask so as to conduct supporting-operation on a carrier. After that, the content of the flask was sufficiently washed with dehydrated heptane. Further, 1.16 ml (1.06 mol) of titanium tetrachloride was added to the flask, and then the flask was stirred for two hours at 110°C so as to conduct the second supporting-operation on a carrier. After that, the content of the flask was sufficiently washed with dehydrated heptane to obtain a solid titanium-based Ziegler-Natta catalyst component having a supported amount of titanium on a carrier of 1.21% by weight.

13. Experiment: Comparative Example 1

Polymerization of 1-octadecene using the Solid Titanium-based Ziegler-Natta Catalyst Component described above

A 1-L autoclave was heat-dried, and thereto were added 200 mL of heptane, 200 mL of 1-octadecene (C_{18}), 2 mmol of triisobutylaluminum and 0.5 mmol of cyclohexylisobutyldimethoxysilane. After the autoclave was stirred and heated up 80°C, 10 μ g mol of, in terms of a titanium atom, the above obtained solid titanium-based Ziegler-Natta catalyst component was added to the autoclave. Then, hydrogen was introduced into the autoclave at 0.8 MPa, and the polymerization reaction was conducted at the polymerization temperature of 80°C for 120 minutes.

After completion of the polymerization reaction, operation of the re-precipitation was repeated using acetone to deposit a reaction-product, which was dried by heating under a reduced pressure to obtain 62 g of a higher α -olefine (C_{18}) polymer (3).

M2 of the obtained higher α -olefin polymer (3) was 91.8 mol % and Tm was 36.9°C and 68.1°C, as shown in Table A below.

14. Experiment: Comparative Example 2

Polymerization of 1-octadecene using the Solid Titanium-based Ziegler-Natta Catalyst Component described above

A 1-L autoclave was heat-dried, and thereto were added 200 mL of heptane, 200 mL of 1-octadecene (C_{18}), 2 mmol of triisobutylaluminum and 0.5 mmol of cyclohexylisobutyldimethoxysilane. After the autoclave was stirred and heated up 120°C, 10 μ mol of, in terms of a titanium atom, the above obtained solid titanium-based Ziegler-Natta catalyst component was added to the autoclave. Then, hydrogen was introduced into the autoclave at 0.9 MPa, and the polymerization reaction was conducted at the polymerization temperature of 120°C for 60 minutes.

After completion of the polymerization reaction, operation of the re-precipitation was repeated using acetone to deposit a reaction-product, which was dried by heating under a reduced pressure to obtain 25 g of a higher α -olefin (C_{18}) polymer (3).

M2 of the obtained higher α -olefin polymer (4) was 87.2 mol % and T_m was 35.1°C and 66.1°C, as shown in Table A below.

15. Experiments: Examples 3 and 4 and Comparative Examples 3 and 4

Preparation and Evaluation of the Thermoplastic Resin compositions

The thermoplastic resin compositions were prepared in the following manner. An amount of a polypropylene homopolymer having MFR of 30 g/10 min. as the thermoplastic resin and a higher α -olefin polymer (1), (2), (3) or (4) prepared in the above Examples 1 and 2 and Comparative Examples 1 and 2 shown in the following Table B, were introduced to a flask such that the total mass of the components was 5 g, and 250 mL of o-dichlorobenzene was added thereto and stirred at 140°C to dissolve the components.

The components were precipitated in methanol, and thus-obtained composition was air-dried and then vacuum-dried each.

The composition was formed by melting compression molding at 230°C, and rapidly cooled with iced water, to obtain a 100- μ m-thick sheet and a 200- μ m-thick sheet.

The sheets were heat-treated at 60°C for 24 hours in a high temperature bath to prepare samples.

The 200- μ m-thick sheet was used for the measurement of miscibility (R) and the 100- μ m-thick sheet was used for the film impact strength measurement.

The results of the measurement of miscibility (R) and film impact strength of the obtained sheets comprising the thermoplastic resin compositions are shown in the following Table C.

16. Table A

| | Higher α -Olefin Polymer | Catalyst | Stereoregularity Index M2 (mole %) | Melting Point(s) ($^{\circ}$ C) |
|-------------|---------------------------------|---------------|------------------------------------|----------------------------------|
| Ex. 3 | Polymer (1) | Metallocene | 60.4 | 41.5 |
| Ex. 4 | Polymer (2) | Metallocene | 50.8 | 40 |
| Comp. Ex. 3 | Polymer (3) | Ziegler-Natta | 91.8 | 36.9 and 68.1 |
| Comp. Ex. 4 | Polymer (4) | Ziegler-Natta | 87.2 | 35.1 and 66.1 |

17. Table B

| | Polypropylene homopolymer | Higher α -olefin polymer | |
|-----------------------|---------------------------|---------------------------------|-------|
| | wt. % | Type | wt. % |
| Example 3 | 70.0 | Polymer (1) | 30.0 |
| Example 4 | 70.0 | Polymer (2) | 30.0 |
| Comparative Example 3 | 70.0 | Polymer (3) | 30.0 |
| Comparative Example 4 | 70.0 | Polymer (4) | 30.0 |

18. Table C

| | Miscibility (R) | Film Impact Strength (kJ/M) |
|-----------------------|-----------------|-----------------------------|
| Example 3 | 1.14 | 6.9 |
| Example 4 | 1.15 | 6.8 |
| Comparative Example 3 | 1.06 | 2.8 |
| Comparative Example 4 | 1.07 | 2.6 |

19. As shown by the comparative experimental data presented in Table C, the thermoplastic resin composition comprising the higher α -olefin polymer (1) of Example 3, which was polymerized using a metallocene catalyst and has a stereoregularity index M2 of 60.4 mole % and a single melting point (T_m) of 41.5 $^{\circ}$ C, and the thermoplastic resin composition comprising the higher α -olefin polymer (2) of Example 4, which was polymerized using a metallocene catalyst and has a stereoregularity index M2 of 50.8 mole % and a single melting point (T_m) of 40 $^{\circ}$ C, exhibit superior properties with respect to increased film impact strength and improved miscibility between the higher α -olefin polymer and the thermoplastic resin.

20. In contrast, the thermoplastic resin composition comprising the higher α -olefin polymer (3) of Comparative Example 3, which was polymerized using a solid titanium-based Ziegler-Natta catalyst and has a stereoregularity index M2 of 91.8 mole % and two melting points (T_m) of 36.9°C and 68.1°C, and the thermoplastic resin composition comprising the higher α -olefin polymer (4) of Comparative Example 4, which was polymerized using a solid titanium-based Ziegler-Natta catalyst and has a stereoregularity index M2 of 87.2 mole % and two melting points (T_m) of 35.1°C and 66.1°C, exhibit inferior properties with respect to decreased film impact strength and reduced miscibility between the higher α -olefin polymer and the thermoplastic resin.

21. This evidence clearly demonstrates that a thermoplastic resin composition comprising a higher α -olefin polymer polymerized using a metallocene catalyst and having a stereoregularity index M2 of ≥ 50 mole % and a single melting point (T_m) of 0°C to 100°C exhibits superior properties with respect to increased film impact strength and improved miscibility between the higher α -olefin polymer and the thermoplastic resin, as compared to the inferior properties exhibited by a traditional thermoplastic resin composition comprising a higher α -olefin polymer polymerized using a conventional Ziegler-Natta catalyst and having two molting points.

22. The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

Shinichi Yukiwasa
Signature

February 13, 2009
Date